BLEACHING COTTON - SEED OIL

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ARMOUR INSTITUTE OF TECHNOLOGY

1912

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Bleaching cotton-seed oil
with American fullers Earth

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A THESIS
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"BLEACHING COTTON-SEED OIL WITH AMERICAN FULLERS EARTH"

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BIBLIOGRAPHY

H. Ries "Clay-Its Occurence, Uses and Properties" 1908.

C.L.Parsons "Fullers Earth" Journal American Chemical Society, April, 1907/

J.T. Porter "Properties and Tests of Fullers Earth" U.S. Geological Survey.

The purpose of this investigation is to study the phenomena of bleaching with fullers earth with the object in view of using the American product in cotton seed oil refining.

The property of removing coloring matter from vegetable oil possessed by certain clays, has not been thoroughly investigated. The theory that magnesium was in some way responsible for bleaching has been proven false. Ries advanced the theory that hydrated silica accounted for much of the bleaching. C.L. Parsons believes that the phenomena is one of simple absorption, since the coloring matter is taken from the earth by alcohol. after the oil has been removed by gasoline.

Porter has performed many experiments on fullers earth with the purpose of finding the active constituents. He discovered that treatment with sodium carbonate did not alter its efficiency, while treatment with sodium hydrate caused it to lose most of its bleaching properties. From the first fact, he showed that hydrous silica did not account for the bleaching since boiling sodium carbonate as well as sodium hydrate removed it. Sodium hydrate also removed considerable alumina. He explains the action of hydrochloric acid, by the fact that it increases the colloidal content.

From these and other facts, Porter drew up the following conclusion."Bleaching is due to a series of hydrated aluminum silicates having an amphorous colloidal structure".These compounds absorb and retain organic coloring matter, thus bleaching the oil.

The part played by colloids is very important, With the purpose of substantiating Porter's theories, and also to discover what treatment would increase the efficiency of the colloids, the fullers earths were treated systematically with various reagents.

The American product is inferior to the English in several respects. Ries gives the following requirements necessary for an American earth to be as good as an English earth.

1. It must bleach as well.
2. It must filter as well.
3. It must absorb no more oil.
4. It must not burst into flames on opening the filter press.
5. It must not impart a bad odor or taste to the oil.

The earths employed in this investigation were typical of the English and American types. The English was a light, cream color; the American a grayish color. The analysis of the English earth is as follows;

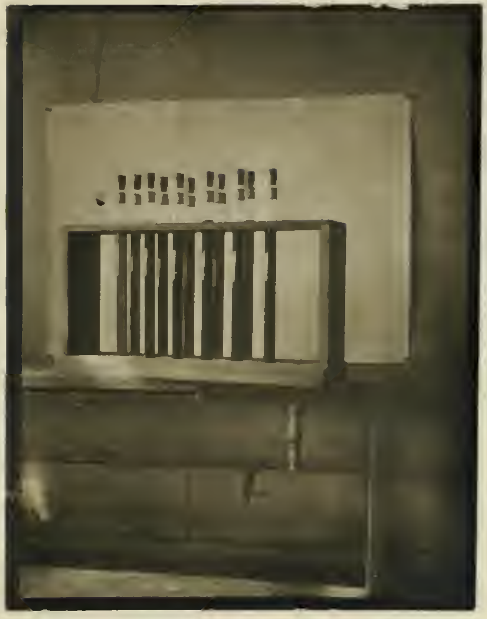
Silica	54.6%
Ferric Oxide	4.46
Alumina	18.24
Lime	4.8
Magnesia	4.7
Moisture	10.16
Total	96.96%

The American earth was one that had been pronounced as unfit for practical work, Before any bleaching tests were made, a set of standards were made up as follows;- The first (#1) was a clear highly refined cotton seed oil; the last (#11) was a crude oil. The intermediate ones consisted of various proportions of the two

Number of Standard	1	2	3	4	5	6	7	8	9	10	11
Parts of Refined Oil	10	9	8	7	6	5	4	3	2	1	0
Parts of Crude Oil	0	1	2	3	4	5	6	7	8	9	10

These standards were placed in 50 C.C. Nessler tubes stoppered well, and kept in racks for comparison.

Bleaching tests were made by heating 50 c.c.of crude oil in a 100 c.c. beaker to 105° C., adding the fullers earth and stirring for 5 minutes. The oil was then filtered thru a dry asbestos mat in a gooch filter and the colors of the oil compared to the proper standard.



THE SET OF STANDARDS.

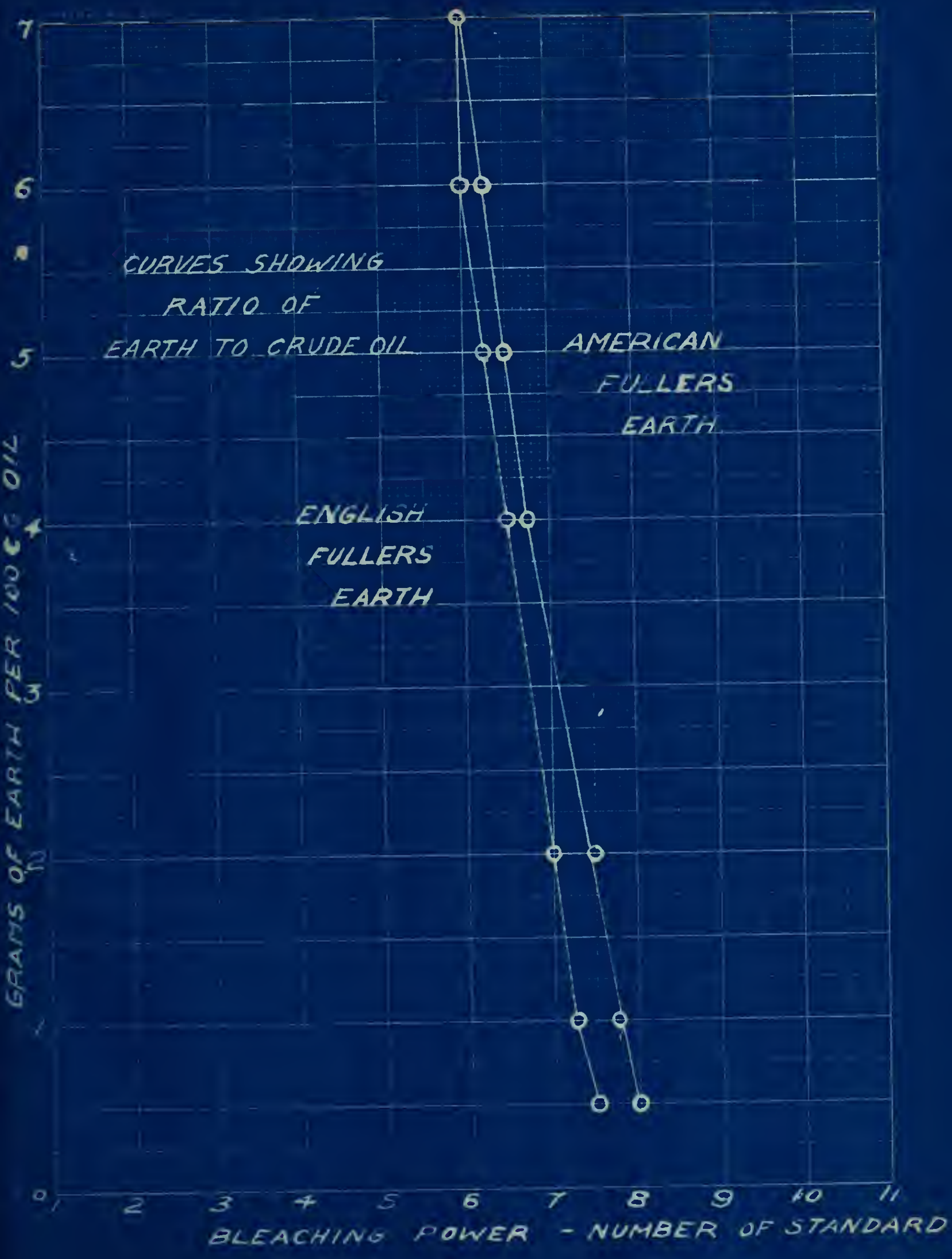
In order to obtain the best proportion of earth to oil in these tests, a series of tests was made having the following amounts

Grams of Earth	25	.50	1.	2.	2,5	3.	3.5
C.C. Crude Oil	50	50	50	50	50	50	50

Both English and American earths were used. The results of this series were as follows;-

Grams of Earth per 100 C.C. Oil	.5	1.	2.	4.	5.	6.	7.
Bleaching Power) American	8	7¾	7½	6¾	6½	6¼	6
N# of Standard)English	7½	7¼	7	6½	6¼	6	6

Comparison of colors were made in a colorimeter.


CURVES SHOWING
RATIO OF
EARTH TO CRUDE OIL
AMERICAN
FULLERS
EARTH
ENGLISH
FULLERS
EARTH
GRAMS OF EARTH PER 100 CC OIL
7
6
5
4
3
2
1
0
1
2
3
4
5
6
7
8
9
10
11
BLEACHING POWER - NUMBER OF STANDARD

From these results, it can be seen that the bleaching power of 0.5 grams per 100 C.C. oil is nearly as much as 7 grams per 100 C.C oil. Hence to make the most sensitive comparative tests of the bleaching power of the earths, the smaller amount should be used. This is proven again by the fact that with 7 grams per 100 C.C., the bleaching power of the two earths is the same; while with 0.5 grams per 100 C.C., there is a very noticable difference. Therefore).25 grams per 50 C.C. oil were used in making the tests.

In order to confirm Porter's theory and also to discover whether there is any increased efficiency to be obtained, both the English and American earths were treated with various chemical reagents. A series of treatments were made with various amounts of hydrochloric acid. In each case 10 grams of earth was treated with 100 C C. hydrochloric acid solution(various strengths Five samples of each earth were prepared, using 0.1%, 0.5%, 2% 6% and 10% H.Cl solution. After washing the samples free of acid they were dried in anoven at 105° C.

In a similar manner a set of samples was prepared, using Na O H of strengths 5%, 2%. 1% and 0.5%.

$K_2 Cr_2 O_7$ and $H_2 SO_4$ were used of strengths 1%, 2%. 3% and 5%.

HNO_3 was used of strengths 1%, 2 %, 5 % and 10%.

H_2, SO_3 was used of strengths 1%, 2 %,5% and 10%.

Al $(OH)_3$ was used by precipitating it in the earths with $Al_2 (SO_4)_3$ and Na OH. Four samples were prepared as follows;

C.C. 20% Na OH	1	2	6.25	12.5
C.C. $Al_2 (SO_4)_3$	2	4	12.5	25.
Grams Al $(OH)_3$	.125	.25	.8	1.6
% Al.$(OH)_3$	1.25	2.5	8.	16.

Ten grams of earth was used in each case.

$Al_2(SiO_3)_3$ was used by precipitating it in the earths, with $Al_2(SO_4)_3$ and Na_2SiO_3. Four samples were prepared as follows;-

C.C. $Al_2(SO_4)_3$	.4	1	2	4
C.C. Na_2SiO_3	.6	1.5	3	6
Grams $Al_2(SiO_3)_3$	0.2	0.5	1.	2.
% $Al_2(SiO_3)_3$	2	5	10	20

Earths were also treated with a saturated soltution of lime and a 1% solution of tannin.

A sample was also prepared by extracting with alcohol and gasoline.

In general the earths treated with acids and salts, were very easily washed by decantation, due to the fact that these reagents caused the colloidal matter to floculate. On the other hand, sodium hydrate caused a gelatin ization on washing which was more noticable as the solutions became more dilute. The cause of this phenomena was the fact that caustic soda attacks alumina compounds, rendering them slimy, and thus increasing the colloidal content.

It is to be noted that electrolytes especially strong acids and bases tend to floculate the earth. This explains why strong caustic did not cause a gelatinization until it was partially washed out.

The question now arises; is there any relation between the colloidal content and the bleaching power. From the bleaching tests which follow, we shall attempt to answer this question.

HCL TREATMENT

ACID.

% HCL.	.1	.5	2.	6.	10.
COLOR WITH AMERICAN.	8	8	8	$7\frac{3}{4}$	$7\frac{1}{2}$
COLOR WITH ENGLISH.	$7\frac{1}{2}$	$7\frac{1}{2}$	$7\frac{1}{2}$	$7\frac{1}{2}$	$7\frac{1}{2}$

NaOH TREATMENT

ALKALI

% NaOH	.5	1.	2.	5.
AMERICAN	8	8	8	$8\frac{1}{2}$
ENGLISH	$7\frac{1}{2}$	$7\frac{1}{2}$	$7\frac{1}{2}$	8

$K_2Cr_2O_7 + H_2SO_4$

OXIDATION.

% OF EACH	1.	2.	3.	5.
AMERICAN	8	8	8	8
ENGLISH	$7\frac{1}{2}$	$7\frac{1}{2}$	$7\frac{1}{2}$	$7\frac{1}{2}$

HNO_3 TREATMENT.

ACID.

% HNO_3	1.	2.	5.	10.
AMERICAN	8	8	8	$7\frac{1}{2}$
ENGLISH	$7\frac{1}{2}$	$7\frac{1}{2}$	$7\frac{1}{2}$	$7\frac{1}{2}$

H_2SO_3

REDUCTION

% H_2SO_3	1.	2	5.	10.
AMERICAN	8	8	8	8
ENGLISH	7½	7½	7½	7½

$Al(OH)_3$

COLLOID

% $Al(OH)_3$	1.25	4.25	8.	16.
AMERICAN	8	8	8¼	8½
ENGLISH	7½	7¾	8	8

Al_2SiO_3

COLLOID

% $Al_2(SiO_3)_3$	2.	5.	10.	20.
AMERICAN	8	8¼	8½	8½
ENGLISH	7½	7[illegible]	8	8

REAGENT	AM.	ENG.
	COLOR	COLOR
$Ca(OH)_2$	8¼	7¾
TANNIN	BLACK	BLACK
SOLVENT	8	7½

From the foregoing results, several conclusions maybe drawn. First, treatment with acids, gave a little higher efficiency especially in the case of hydrochloric acid. Lime and Alumina were removed to some extent by the acid, while large amounts of iron were dissolved out as indicated by the deep yellow color of the solution obtained. According to Ries, acid may increase the colloidal content of the earth; this was noticable from the increase in volume of the earth when electrolytes were washed out.

Sodium hydrate, altho increasing the colloidal matter materially in water solution, really impaired the bleaching qualities in oil. This may be due to the fact that on drying the colloidal matter reverted to its original form; also that certain alumino silicates were attacked and changed in form, thus lowering their bleaching power.

Oxidizing and reducing agents had no effect. Lime water hindered the bleaching action. Tannin, which according to Acheson deflocculates clays, did not improve the earth. Any slight additional bleaching by the earth would have been counterbalanced by the darkening of the oil by the Tannin. Solvents had no effect showing that the bleaching was not due to organic matter.

Additive colloidal matter, such as Aluminum hydrate or silicate did not have sufficient bleaching power of their own to improve the earth.

In brief the results showed that the bleaching power depends primarily on colloids; but, owing to the different forms in which they exist, there is no direct relationship bewteen the amount of colloid and the efficiency of the earth.

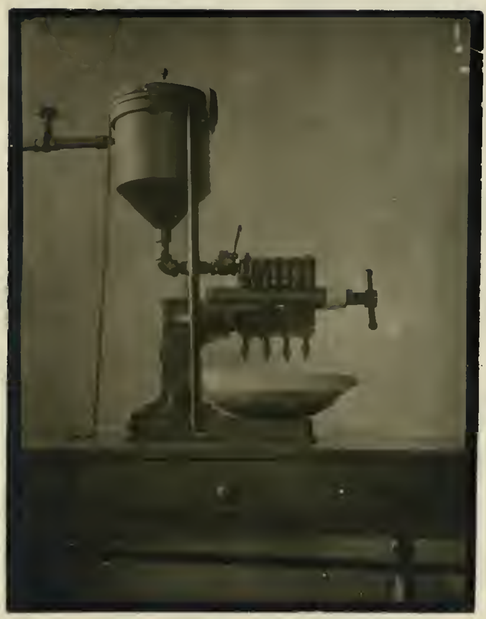
The bleaching powers of a fullers earth are not easily improved. The only beneficial treatment found was with hydrochloric acid, and this may not always be satisfactory although it may remove some objectional matter. The substance that ordinarily effects colloids, do not alter the bleaching power of fullers earth.

To improve the bleaching power was a problem that was unsolved and which probably cannot be solved.

Besides being deficient in bleaching power, American fullers earth may not filter as well as the English, may absorb more oil; become overheated in the press; or impart a bad taste or odor to the oil.

To investgate these shortcomings, a small filter press was installed. It consisted of a small monte-jus of two and one half liters capacity, and three circular frames of a capacity of 350 grams of press cake each. A thermometer cup was placed in the first frame this frame being the only one used. Canvas duck filter cloths were used and found satisfactory. Air pressure of 60 lbs. was used throughout.

The oil used was the same as that employed in practice. The crude oil was treated with sodium hydrate and the foots settles out. In order to find the ratio of sodium hydrate to oil to be used a series



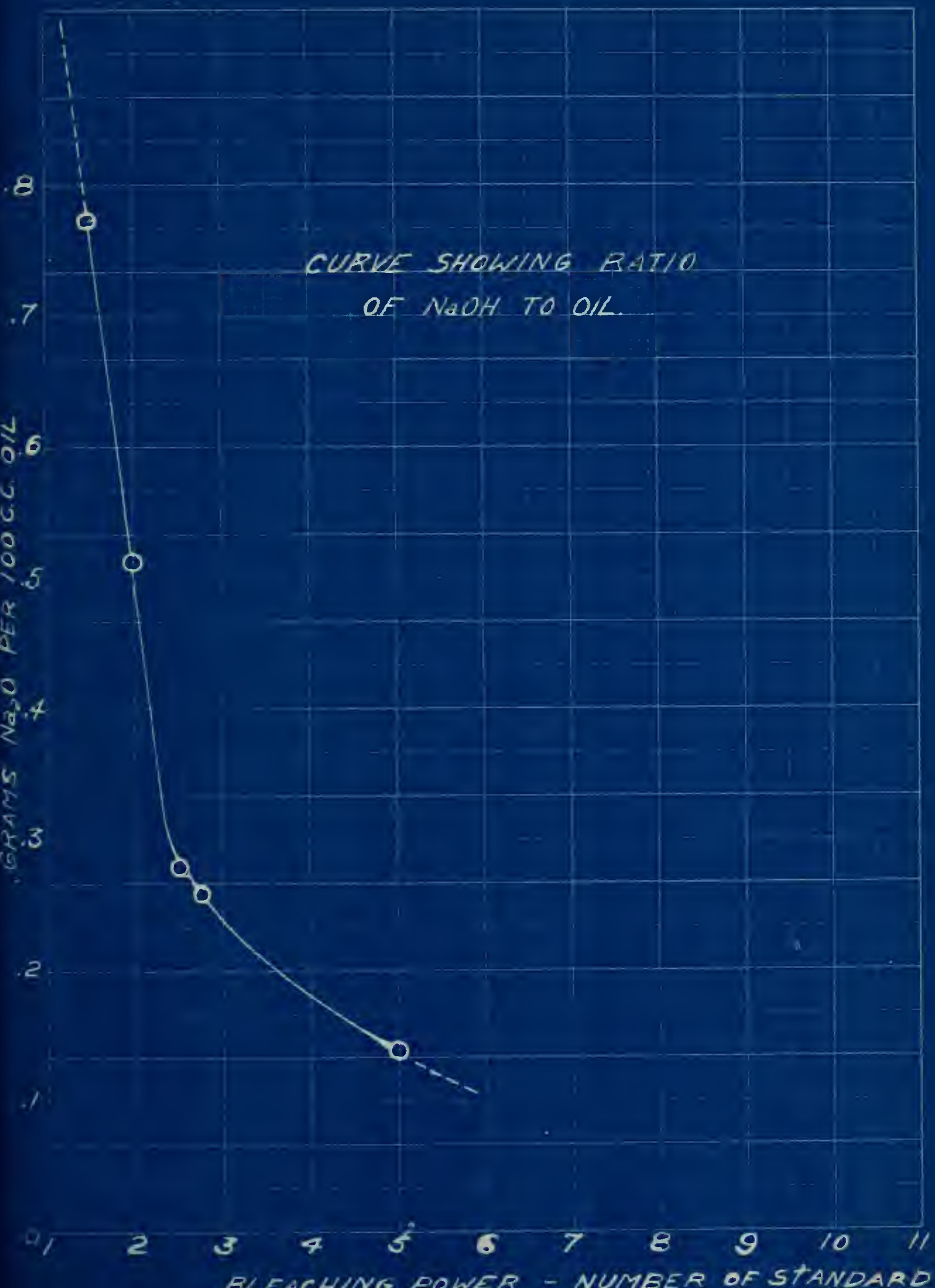
THE FILTER PRESS.

of oils were prepared on a small scale using verying amounts of caustic. The method of treating the oil consisted of heating 50 C.C. in a small beaker to 105°, dropping in the desired amounts of 12° or 20° Be. caustic, stirring for five minutes, and then filtering through dry asbestos. The colors of the filtrates were then compared with the standards. All samples were done in duplicate, and agreed very closely.

	12° Be'		20° Be'		
Na OH	1 C.C.	2 C.C.	1 C.C.	2 C.C.	3 C.C.
COLOR	5	2½	2¾	2	1½

Calculated

Na_2O per 100 C.C. oil	Color
.136	5
.272	2½
.256	2¾
.512	2
.768	1½

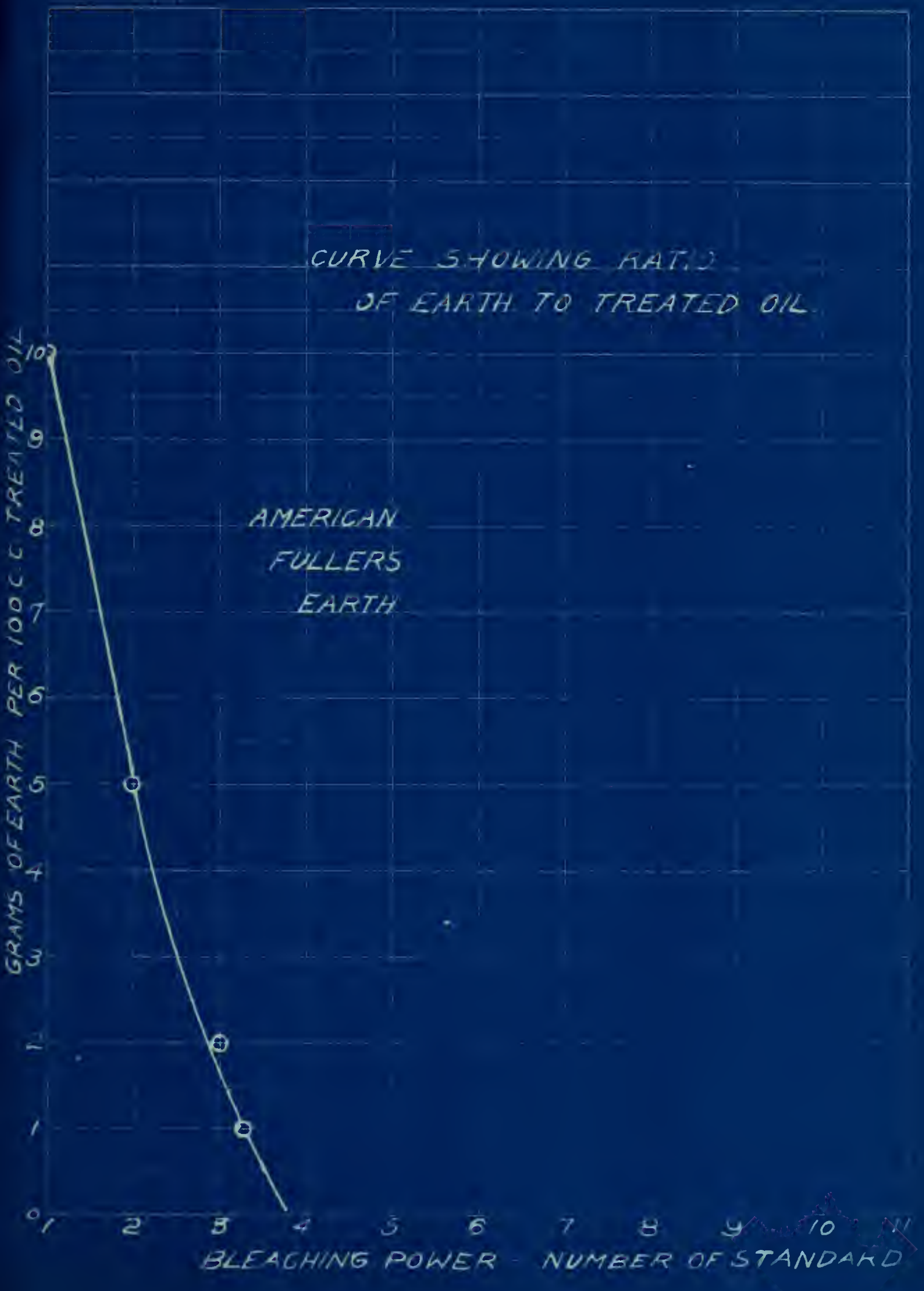

CURVE SHOWING RATIO
OF NaOH TO OIL.
GRAMS Na$_2$O PER 100 C.C. OIL
.8
.7
.6
.5
.4
.3
.2
.1
0
1
2
3
4
5
6
7
8
9
10
11
BLEACHING POWER - NUMBER OF STANDARD

From the curve, it was decided that 2 C.C. of 20° Be', caustic was sufficient, In making this oil up in quantity, ten liters were heated up at a time to 110° C, and 400 C.C. of 20° Be' caustic added slowly with constant stirring. After settling over night, the oil was tapped off ready for use. Its color was a little darker than was expected. Probably this was due to the fact that stirring was more thorough in the small beaker, thus bringing the sodium hydrate into more intimate contact with the oil. The foots of two different lots of oil were 2.41 lbs. and 2.3 lbs. The % foots is therefore 12% which is very high, showing a rather poor grade of crude oil.

Next, to find the effect of adding different amounts of the American earth to this treated oil, a series of runs was made using 50 C.C. oil, as before and various amounts of the fullers earth

Results were

Gr. of Earth	.5	1.	2.5	5.
Gr. of Earth per 100 C.C. Oil	1.	2.	5.	10.
Color	3¼	3	2	1


CURVE SHOWING RATIO
OF EARTH TO TREATED OIL
AMERICAN
FULLERS
EARTH
GRAMS OF EARTH PER 100 C.C. TREATED OIL
0
1
2
3
4
5
6
7
8
9
10
1
2
3
4
5
6
7
8
9
10
11
BLEACHING POWER NUMBER OF STANDARD

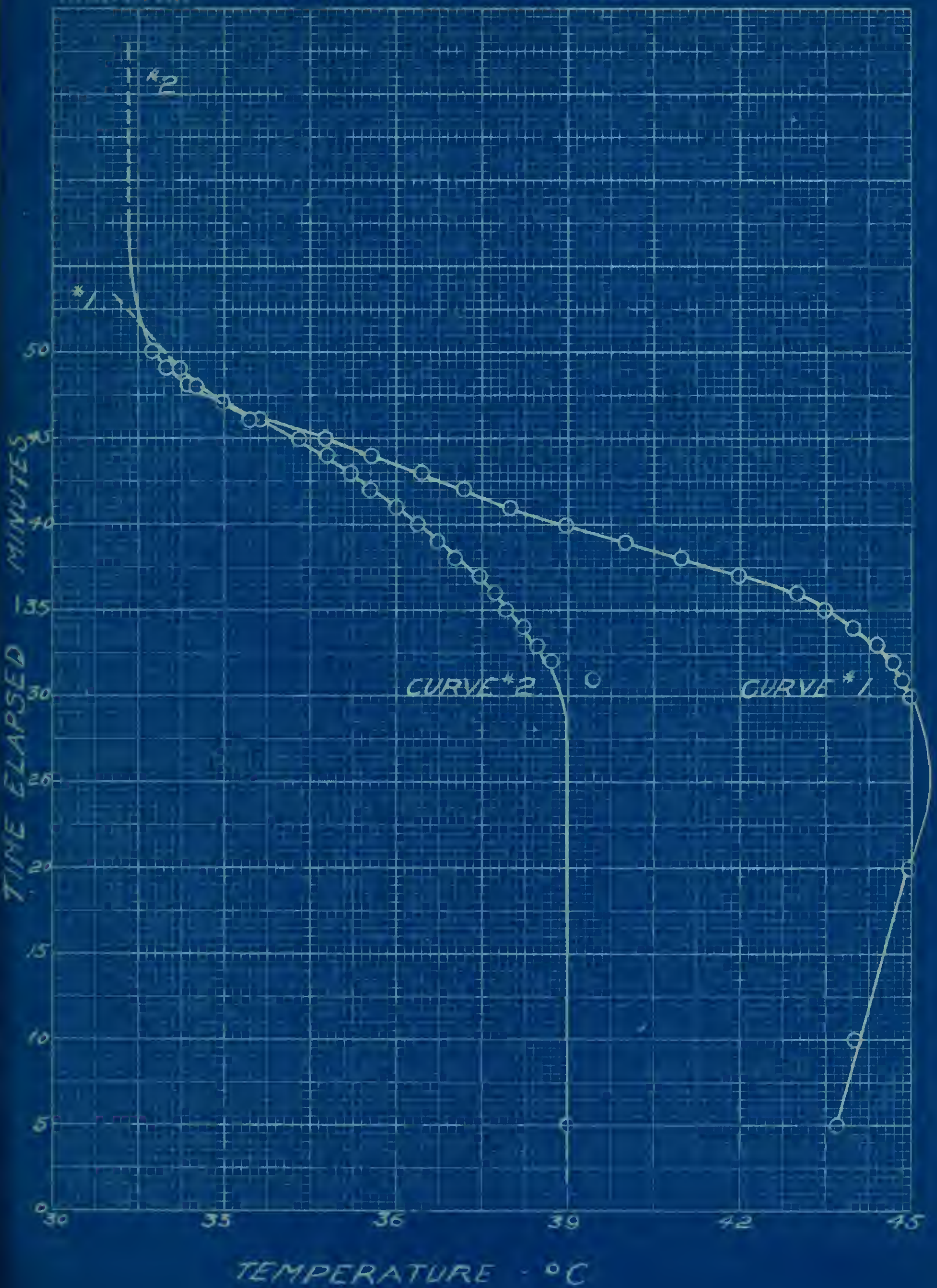
From this curve it can be seen that the coloring matter removed is nearly directly proportionate to the amount of earth used In practice, 5 % earth is considered sufficient. But owing to the small capacity of the monte-jus and the relatively large capacity of the frame, 10% and 12½% were used in the runs on the small filter press.

Two runs were made to discover any rise in temperature due to the American earth. The method employed was as follows, 2500 C.C. of treated oil were heated in an agate dish to 110° C and all gases driven off. 325 grams of American earth were then added and stirred for five minutes, the temperature being maintained at 105° C. It was then poured quickly into the monte-jus and filtered Readings are shown on the data sheet. The curve shows more clearly the fall in temperature during filtration and while the air is being blown through. In the plants where trouble was reported from spontaneous combustion of the press cake on leaving the press the cake had already been highly heated by the blowing thru of air. No such rise was observed with this earth. A slight heat was however generated as shown by the high temperature (31°C) after air had blown through all night. From this, we conclude that there is no excessive rise in temperature to be expected from this earth, if proper precautions are taken.

TEMPERATURE DATA

#1.		#2	
TIME (MIN) ELAPSED	TEMP. C.	TIME (MIN.) ELAPSED	TEMP. °C
5	43.8	5	39.0
10	44.	31	39.5
20	45.	32	38.7
30	45	33	38.5
31	44.9	34	38.3
32	44.7	35	38.0
33	44.4	36	37.7
34	44.0	37	37.5
35	43.5	38	37.0
36	43.0	39	36.8
37	42	40	36.4
38	41.	41	36.0
39	40	42	35.6
40	39.	43	35.2
41	38	44	34.8
42	37.2	45	34.3
43	36.4	46	33.6
44	35.6	47	33.0
45	34.8	48	32.4
46	33.5	49	31.9
47	33.	50	31.75
48	32.5	16 hours	31.5
49	32.2		

TEMPERATURE CURVES



Other runs were then made using the same method of proceadure . First, 200 grams of earth were used then 300, 350, and 400 gr. The purpose of these runs was to measure the time of filtration, note the amount of oil absorbed and retained by press cake, and to examine the color, odor and taste of the filtered oil The results are shown on the following data sheet.

TEST RUNS OF FILTER PRESS.

Nº OF TEST.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
C.C. OF OIL.	2000	2000	2,500	2,500.	2,500	2,500	2,500	2,500	2,500	2,500.
GR. OF EARTH.	200	200	300	300	300	300	300	350	350	400
KIND OF EARTH.	ENG.	AM.	ENG.	AM.	$\frac{1}{2}$ E. + $\frac{1}{2}$ A.	Am. + 25% SiO_2 (80 MESH)	AM. - FINES WASHED OUT	AM.	ENG.	ENG.
C.C. OF FILTRATE.	1900	1900	2,400	2,400	2,400	2,400	2,400	1000	1650	1000.
WT. OF PRESSCAKE.	249	253	380	378	380	360	375	——	——	——
OIL IN PRESSCAKE.	49	53	80	78	80	60	75	——	——	——
TIME START.	9:38	10:14	11:54:15	1:25	3:10	10:09	9:02	10:51	11:03	11:06
TIME GASP.	9:52	10:24	12:07:45	2:08	3:48	10:25	9:16	CLOGGED	CLOGGED	CLOGGED.
TIME END.	9:52	10:29	12:12:45	2:13	3:53	10:30	9:21	11:12	11:31	11:29
TIME OF FILTERING.	9 MIN.	10 MIN.	$13\frac{1}{2}$ MIN.	43 MIN.	38 MIN.	16 MIN.	14 MIN.	NOT COMPLETE	NOT COMPLETE	NOT COMPLETE
COLOR.	1	$1\frac{1}{4}$	0	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{8}$	0	0	0	0
TASTE.	GOOD.	GOOD.	GOOD.	GOOD.	GOOD.	GOOD.	GOOD.	GOOD.	GOOD	FAIR
ODOR.	GOOD.	GOOD.	GOOD.	GOOD.	GOOD.	GOOD.	GOOD.	GOOD.	GOOD	FAIR

From the data, it will be noticed, that no more oil was absorbed by the American than by the English earth; in fact, the oil was absorbed was exactly the same in each case, so that this possible fault does not exist.

As for taste and odor, this is difficult problem since individual preference is here a large factor. The taste imparted by the American earth is of the same nature as that of the English earth, but slightly stronger. This may or may not be objectionable since theclayey flavor tends to neutralize the taste of the oil itself, which is none too pleasant.

Tests Nos. 1 and 2 indicate a slightly greater porosity of the English earth. Only about ½ of the frame was filled however. With 300 grams, where the frame was filled nearly full, the English earth showed marked superiority, taking 13 minutes to filter while the American took forty-three minutes.

There is therefore but one serious objection to the American earth. This is that the fine clayey substance clogs the press. To correct this is a difficult matter. The fines must either be removed, altered so as not to slime, or be mixed with enough porous material to neutralize the clogging effect.

With this in view three samples of the American earth were treated; the first by washing out the fines with water; the second by mixing 25% $Si O_2$ (80 mesh), and the third by adding 50% of the English earth. The times taken for filtration were 14, 16 and 38 minutes respectively, Moreover the oil absorbed by the press was less in the treated samples. As for the color of the oil, it was actually improved by washing out the fines, and practically not affected by the addition of silica. Some of the colors were lighter than #1 standard, so a sample of very light cooking cotton-seed oil was obtained, and labeled #0.

These results show conclusively the trouble with the American earth, and the remedy that should be applied. Either washing out the fines, or adding $Si O_2$, or a combination of these two methods will render the American earth practically as good as the English. The exact method to be adopted, will, of course, depend on the relative economy of these two methods.

We conclude, that in cotton-seed oil bleaching, there is no cause for the use of English earth, except personal prejudice; and by proper treatment, American earth can be used with complete satisfaction.